158429

Sauget data
Due 5/19/82

WRIGHT STATE

Wright State University
Dayton, Ohio 45435

Brehm Laboratory
513/873-2202

May 3, 1982

Mr. Curtis Ross
United States Environmental Protection Agency
Region V
230 S. Dearborn
Chicago, Illinois 60604

RE: EPA Order No. 56606 NAEX

Dear Mr. Ross:

All analyses specified under Tasks 1 and 2 of the subject EPA Purchase Order No. 56606 NAEX have now been completed by our laboratory. As you know, each of the five water/sediment samples were analyzed for CDDs/CDFs as required under Task 1 and these data, as well as a complete description of the analytical methodology employed, were formally transmitted to you in an interim report dated March 16, 1982. Regarding our telephone conversation of March 30, 1982 in which you inquired about precursors of chlorinated dibenzo-p-dioxins (CDDs) which could possibly be present in the Sauget Landfill, it should be emphasized that various compounds are known which are precursors for the CDDs. For example, chlorinated phenoxyphenols, chlorinated phenols, chlorinated benzenes and possibly even polyvinyl chloride polymers have, under certain conditions, been found to give rise to CDDs. In addition, CDDs have been detected in stack effluents arising from municipal waste incineration. Regarding the question of whether or not precursors such as the chlorophenoxyphenols, if present in the environmental sample, could, under conditions of analysis undergo dehydrohalogenation and give rise to CDDs, we feel that if phenoxyphenols were present at concentrations comparable to the concentrations of CDDs which were found in the samples, that the sample clean-up methodology would effectively remove these prior to gas chromatographic-mass spectrometric analysis. The presence of large concentrations of phenoxyphenols (perhaps 100X concentration of CDDs in the sample) could conceivably overwhelm the sample clean-up procedure, but, no specific evidence exists which indicates that large concentrations of phenoxyphenols do indeed generate CDDs during analysis. The phenoxyphenol question should be studied further, but this is difficult at present since well-characterized standards are not readily available. If environmental samples do contain chlorinated phenoxyphenols, it is possible that, under certain conditions which could exist in a chemical landfill, cyclization of these compounds could occur and give rise to CDDs. Here again experimentation is required in order to substantiate this possibility.

The purpose of the present report is to summarize the methodology employed and the results obtained in assaying the five water/sediment samples for the various compounds specified by EPA under Task 2 of the subject purchase order. The samples received for analysis at the beginning of the project are listed in Table 1 and the descriptions listed therein are based upon observations made in this laboratory at the time of receipt of samples. Table 2 lists the organic compounds which were to be determined under Task 2 of the EPA order.

Obviously, several different isomers are possible for some of the compounds listed by EPA, and in these cases, calibrations were accomplished using representative isomers of these compounds, but not all possible isomers. The representative compounds used for calibration and quality assurance purposes are also listed in Table 2. High Performance Liquid Chromatography (HPLC) was employed to detect and quantitate the compounds of interest which were present in extracts of each of the water/sediment samples. The details of the analytical methodology employed are given in the Analytical Protocol appended to this report. The analytical results obtained are discussed below.

Initially, the methodology was verified by accomplishing analyses of standard solutions and when satisfactory results were obtained, actual samples were analyzed along with actual samples which had been spiked with the compounds of interest. Copies of representative chromatograms are attached as Figures 1-7. The data obtained are also listed in tabular form in Table 3. As seen in Table 3, recoveries of the compounds from actual samples prepared to contain known concentrations of the compounds of interest were satisfactory. However, the water/sediment samples themselves were found to contain no detectable levels of the pertinent compounds. These data are not in agreement with the results obtained previously by EPA, which were appended to the EPA order received by Wright State. The concentrations of the pollutants listed by EPA as being detected in similar samples are on the order of 5-10 times the minimum detectable concentrations achieved in the present analyses. The results obtained in the present analyses, therefore, may indicate that the water samples were not adequately preserved at the time of sampling. If appropriate reagents were not added to the water samples at the time of sampling (see, for example, the attached recommendations from Standard Methods For Water and Wastewater Analysis) then microbial degradation of some, if not all, of the compounds of interest could have occurred prior to analysis. The apparent absence of appreciable concentrations of both the pollutants of interest and of any similar compounds tends to further suggest that some degradation of the organic compounds may have occurred. Further analyses of fresh samples (with added preservatives) would indicate whether or not the lack of preservation was a problem with the present samples.

This completes this work called for under EPA Order No. 56606 NAEX. Our invoice is being submitted under separate cover. If you have any questions or comments regarding these data, please don't hesitate to call us. We appreciate this opportunity to work with USEPA on this important project.

Sincerely,

Thomas O. Tiernan, Ph.D.
Professor of Chemistry and
Director of Brehm Laboratory

Michael L. Taylor, Ph.D.
Associate Professor of
Pharmacology/Toxicology and
Associate Director of
Brehm Laboratory

TOT/gdg

TABLE 1

BREHM LABORATORY, WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435

LISTING OF SAMPLES RECEIVED FROM USEPA (CHICAGO, REGION V)[1].

EPA I.D. No.	WSU Sample No.	Description
E1205 82WT06S01	CWS-1	1 gallon of water/sediment
E1206 82WT06S03	CWS-2	3/4 gallon of water/sediment
E1208 82WT06S05	CWS-3	1 gallon of water/sediment
E1207 82WT06S07	CWS-4	3/4 gallon of water/sediment
82WT06R01	CWS-5	3/4 gallon of water/sediment

[1]. Samples were received on January 14, 1982. Samples were packed in styrofoam beads, and ice water was present in shipping containers. Samples CWS-2 and CWS-5 were shipped together in one container and samples CWS-1,-3 and -4 were shipped together in a second container. Caps on bottles were taped.

TABLE 2

BREHM LABORATORY, WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435

SUSPECTED POLLUTANTS AND REPRESENTATIVE COMPOUNDS ANALYZED UNDER TASK #2, EPA ORDER 56606 NAEX

Compounds Listed in Task #2	Representative Compounds Employed in Calibration/QC Studies
1. Chloroaniline	3-Chloroaniline
2. Chloronitrobenzene	1-Chloro-2-nitrobenzene
3. Dichlorophenol	2,4-dichlorophenol
4. 2,4-D	2,4-dichlorophenoxyacetic acid
5. Phenol	phenol
6. Methylbenzosulfaamide	p-toluenesulfonamide
7. Benzoic Acid	benzoic acid
8. Benzene carboxylic acid	
9. Dichloraniline	3,5-dichloroaniline

TABLE 3

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ANALYTICAL RESULTS OBTAINED FOR SUSPECTED POLLUTANTS AND REPRESENTATIVE COMPOUNDS

Suspected Pollutant	WSU Sample No.[1] CWS-1	CWS-2	CWS-3	CWS-4	CWS-5	Spiked CWS-2 Found (added) ng/ml	Spiked CWS-3 Found (added ng/ml
Chloroaniline	ND	ND	ND	ND	ND	--	903(1000)
Chloronitrobenzene	ND	ND	ND	ND	ND	--	3,500(5,090)
Dichlorophenol	ND	ND	ND	ND	ND	900(1030)	--
2,4-D	ND	ND	ND	ND	ND	10,000(11,000)	--
Phenol	ND	ND	ND	ND	ND	900(780)	--
Methylbenzosulfaamide (p-toluenesulfonamide)	ND	ND	ND	ND	ND	1000(640)	--
Benzoic Acid Benzene Carboxylic acid	ND	ND	ND	ND	ND	1000(1050)	--
Dichloroaniline	ND	ND	ND	ND	ND	--	1,290(1000)

1. See Table 1 for the corresponding EPA sample numbers. ND means none detected, the following limits of detection apply:

chloroaniline, dichloroaniline, chloronitrobenzene	250 ng/mL
2,4-D	3000 ng/mL
phenol	500 ng/mL
p-toluenesulfonamide	600 ng/mL
Benzoic acid	500 ng/mL
Dichlorophenol	250 ng/mL

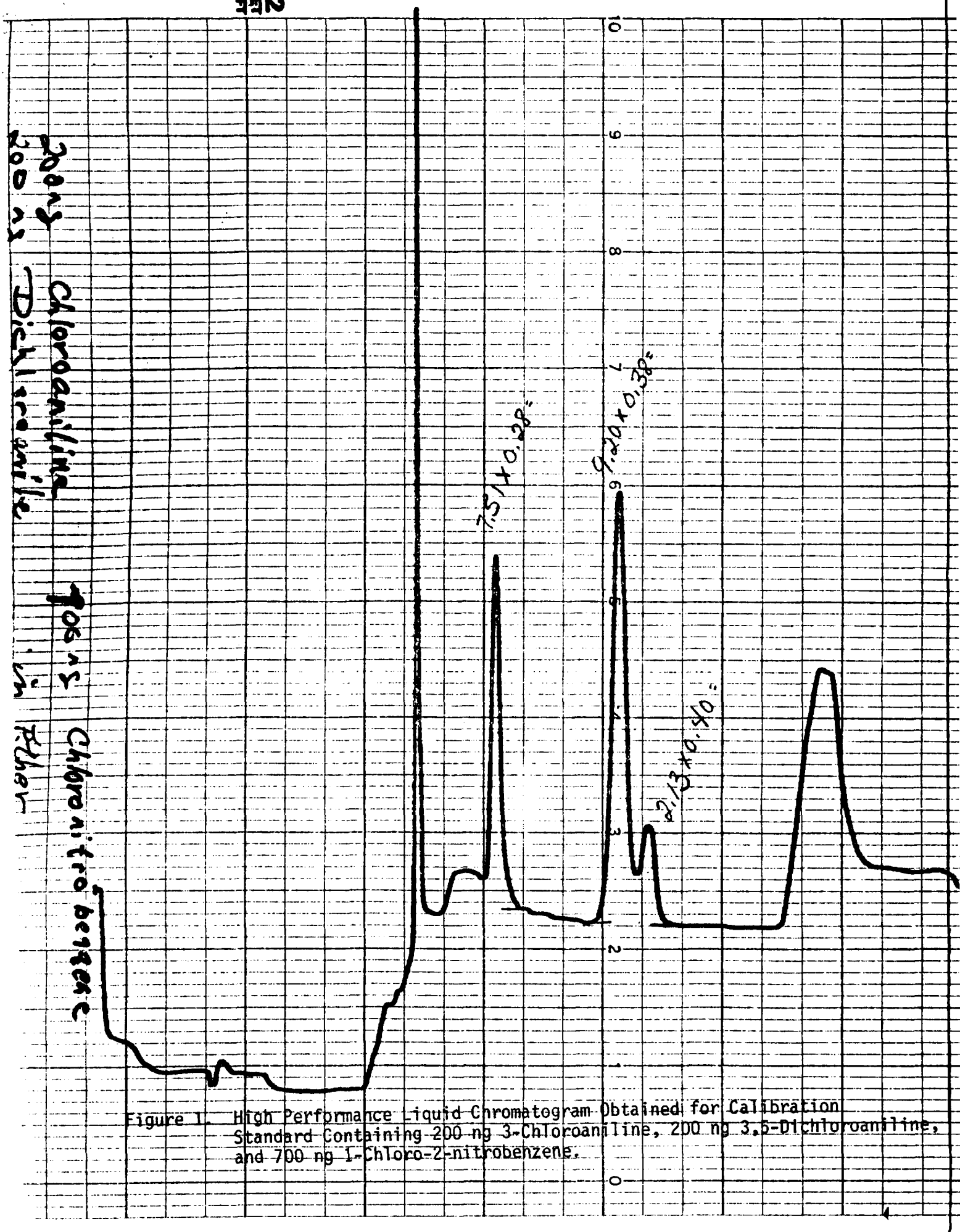


Figure 1. High Performance Liquid Chromatogram Obtained for Calibration Standard Containing 200 ng 3-Chloroaniline, 200 ng 3,5-Dichloroaniline, and 700 ng 1-Chloro-2-nitrobenzene.

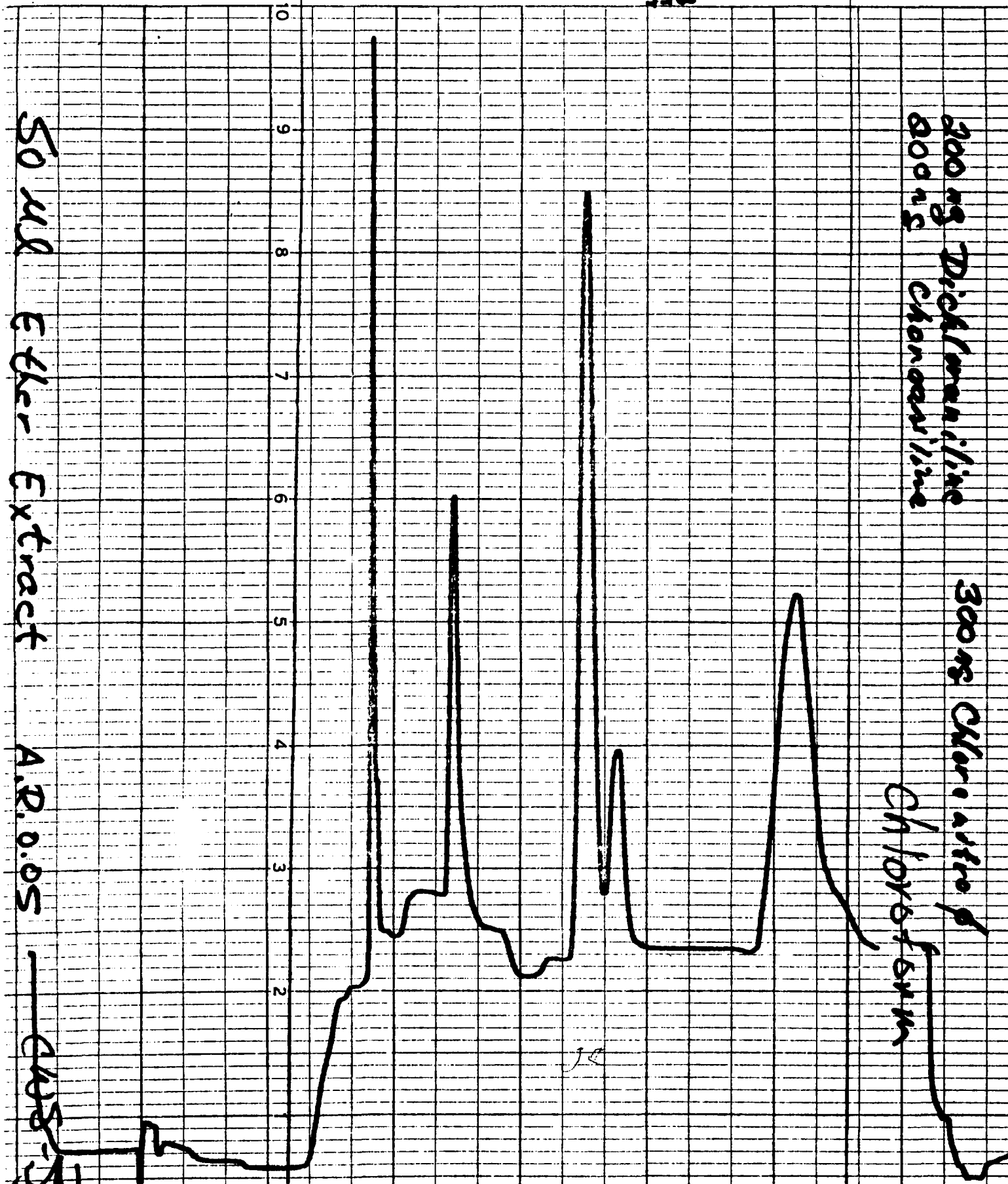


Figure 2. High Performance Liquid Chromatogram Obtained For An Extract of Sample CWS-3 Spiked With 3-Chloroaniline, 3,5-Dichloroaniline and 1-Chloro-2-nitrobenzene.

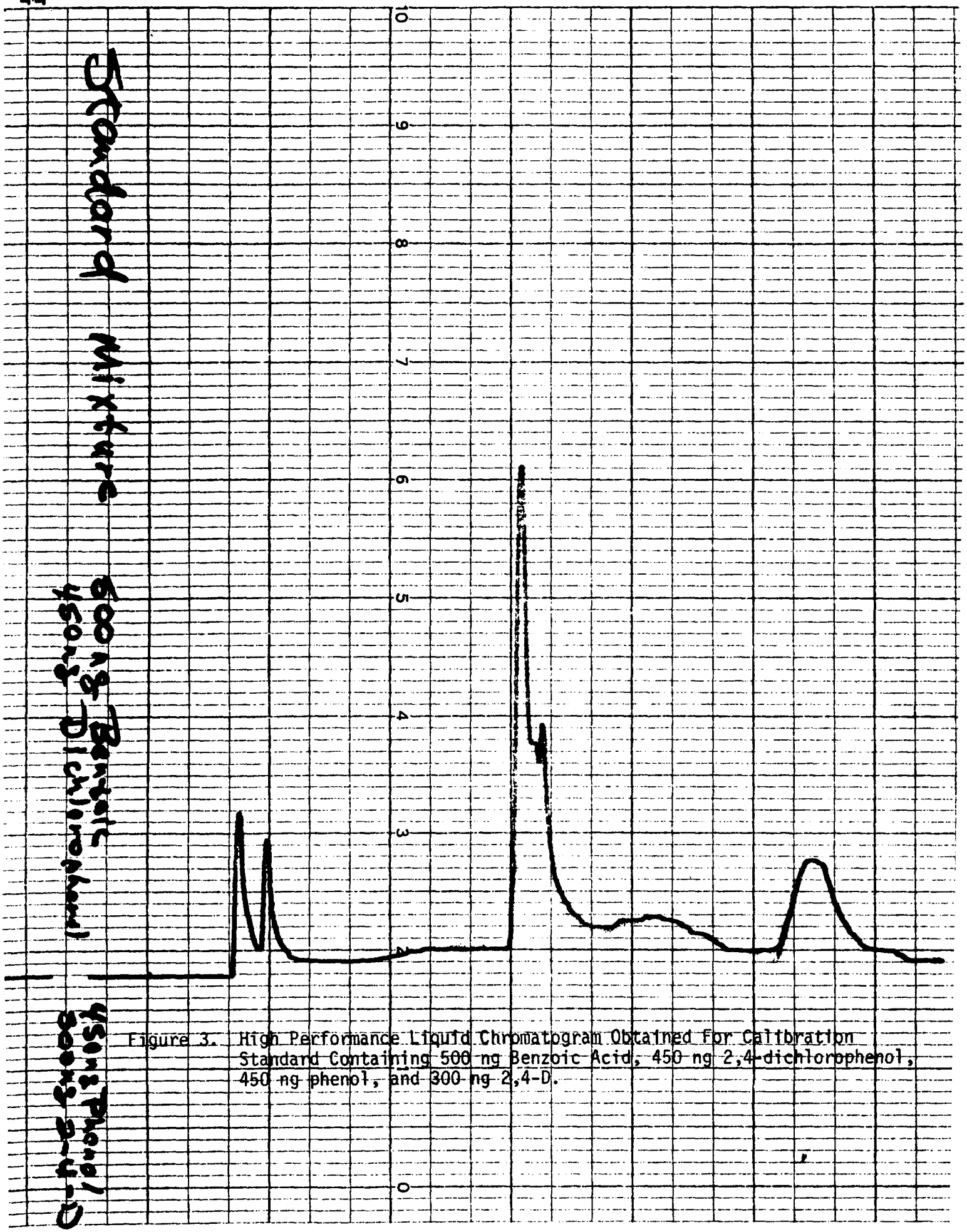


Figure 3. High Performance Liquid Chromatogram Obtained For Calibration Standard Containing 500 ng Benzoic Acid, 450 ng 2,4-dichlorophenol, 450 ng phenol, and 300 ng 2,4-D.

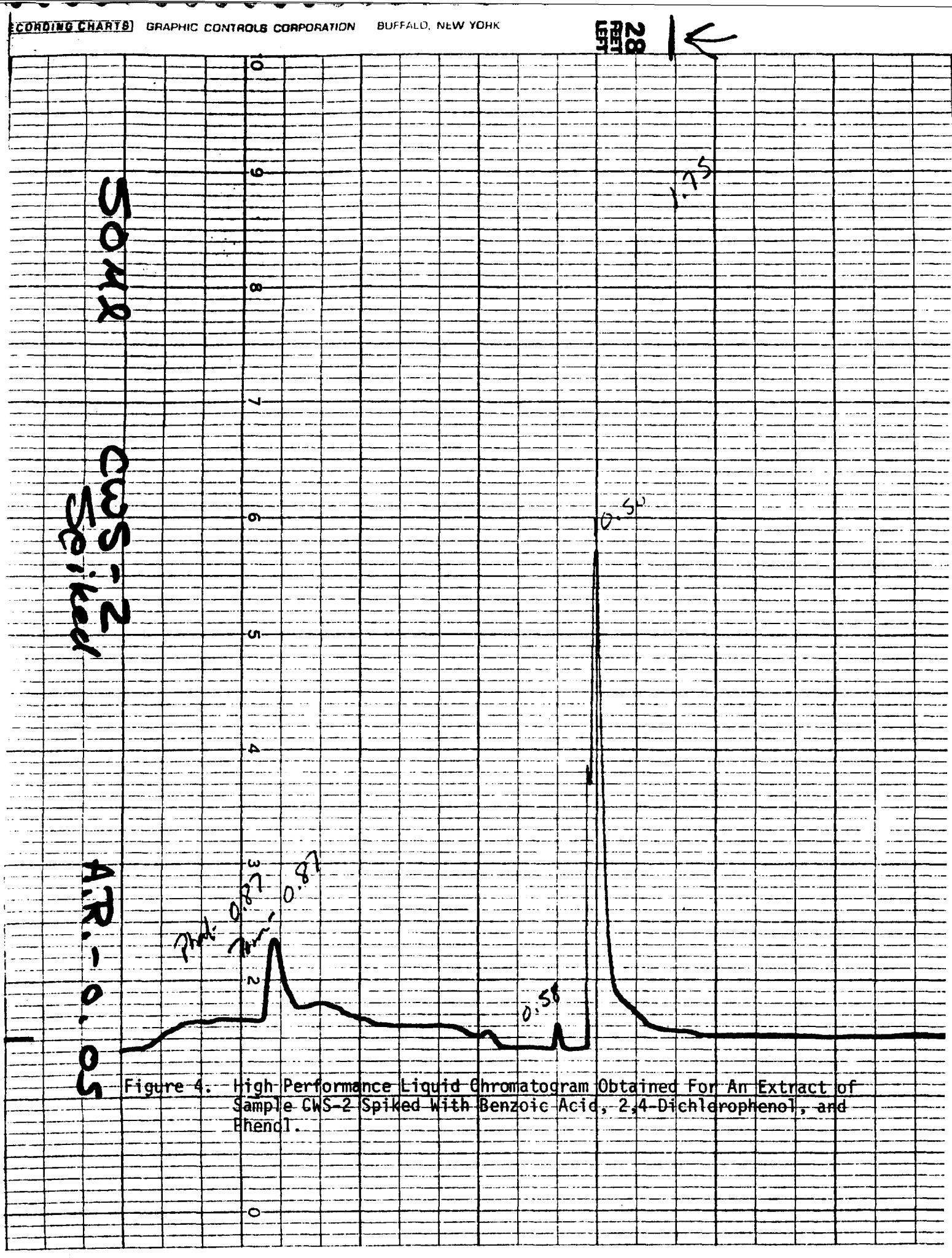


Figure 4. High Performance Liquid Chromatogram Obtained For An Extract of Sample CWS-2 Spiked With Benzoic Acid, 2,4-Dichlorophenol, and Phenol.

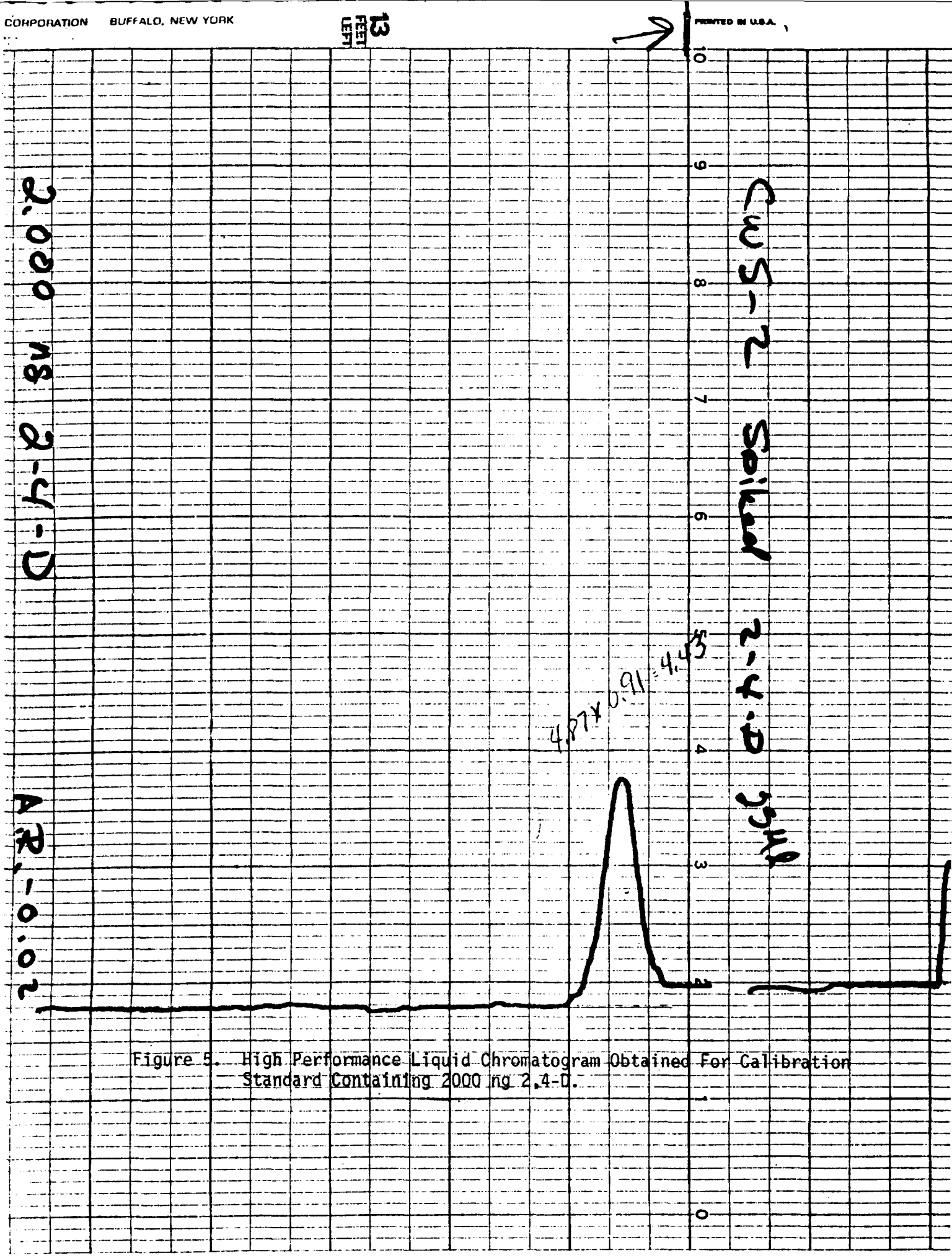


Figure 5. High Performance Liquid Chromatogram Obtained For Calibration Standard Containing 2000 ng 2,4-D.

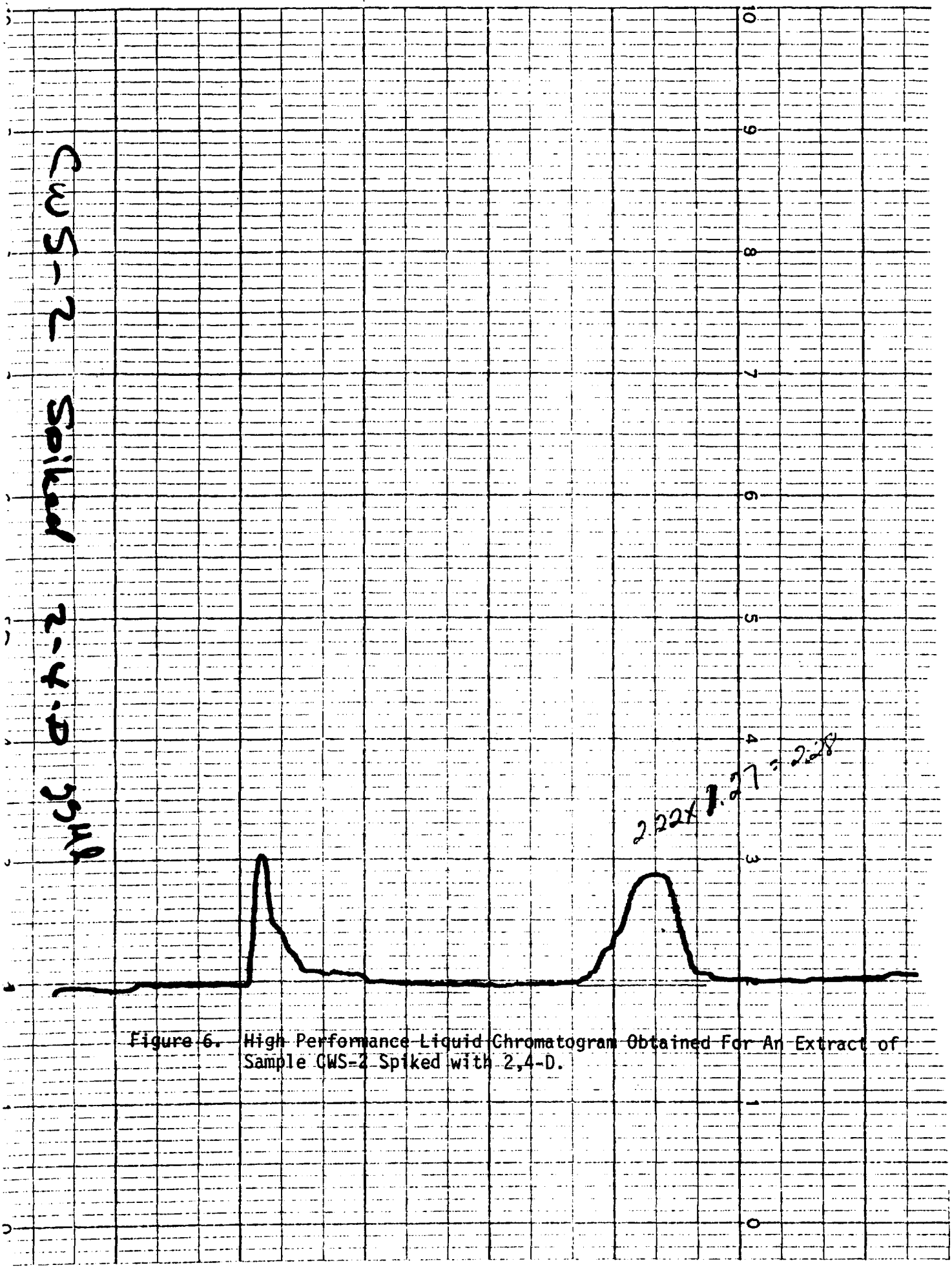


Figure 6. High Performance Liquid Chromatogram Obtained For An Extract of Sample CWS-2 Spiked with 2,4-D.

CWS-2 Seiko

CWS-3 A.R. 0.02 Sorb

Figure 7. High Performance Liquid Chromatogram Obtained For An Extract of Sample CWS-3 (Analyzed As Received).

APPENDIX A

Brehm Laboratory Protocol For Extraction and Analysis of Wastewater Samples For Anilines, Phenols, and Benzoic Acid and Related Compounds

BREHM LABORATORY, WRIGHT STATE UNIVERSITY, DAYTON, OHIO 45435

ANALYTICAL PROTOCOL FOR DETERMINATION OF CHLOROANILINES, PHENOLS AND BENZOIC ACID DERIVATIVES IN WASTEWATER SAMPLES

A. Extraction.

1. Thoroughly mix the water/sediment sample by shaking for about one minute.
2. Immediately transfer a 100 mL aliquot of the sample to a clean, 200 mL flint glass bottle (equipped with Teflon-lined screw cap). For extraction of chloroanilines and chloronitrobenzenes adjust pH to pH 10 by addition of 1-2 mL of 1N aqueous NaOH. For extraction of phenols, benzoic acid and related compounds (2,4-D, p-toluenesulfonamide) adjust the pH of the 100 mL aliquot to pH 2 by addition of 1N HCl.
3. After pH adjustment add 25 mL of diethyl ether and shake for 30 minutes (taking care to periodically relieve pressure in the extraction vessel).
4. Allow the mixture to stand and if incomplete separation of the layers is obtained, add 5 mL of methanol. Separate the layers and retain the ether layer for subsequent analysis.

B. Procedures and Operating Parameters For High Performance Liquid Chromatographic Analysis of the Extracts.

1. High Performance Liquid Chromatography Procedures

   a. Instrumentation: Varian Model 5021 Microprocessor Controlled High Performance Liquid Chromatograph equipped with CDS-111L Data System.

   b. Parameters:

   Pressure: Minimum: 10 atm
   Maximum: 350 atm

   Injection Loop: 50 µl

   Column: Guard: 37 Vydac SC Reverse Phase
   4.0 cm x 0.4 cm I.D.

   Analytical: DuPont Zorbax-ODS
   25.0 cm x 0.6 cm I.D.

Temperature: Guard Column: Ambient
Analytical Column: Ambient

Detector: Fixed UV: 254nm

Dichlorophenol, Phenol, Benzoic Acid, p-Toluenesulfonamide

Time	Code	Value
.0	%	100% 0.1M Phosphate Buffer (pH12)
.0	Flow	2.0 mL/min
.0	Event	Hold
.1	Event	Inject
5.0	%	60% Buffer/40% Methanol
20.0	%	60% Buffer/40% Methanol
25.0	%	100% Buffer
25.0	Flow	2.0 mL/min
30.0	Event	Reset

2,4-D

.0	%	85% 0.1M Phosphate Buffer (pH-12)/ 15% Methanol
.0	Flow	2.0
.0	Event	Hold
.0	Event	Inject
20.0	Event	Reset

Anilines, Chloronitrobenzene

0.0	%	80% 0.15M Phosphate Buffer (pH2.1)/ 20% acetonitrile
0.0	Flow	2.0
0.0	Event	Hold
0.1	Event	Inject

Time	Code	Value
1.0	%	80% Buffer/20% acetonitrile
5.0	%	40% Buffer/60% acetonitrile
15.0	%	40% Buffer/60% acetonitrile
20.0	%	80% Buffer/20% acetonitrile
25.0	Flow	2.0 mL/min
25.0	Event	Reset

C. Analysis/Calibration.

Ten to 50 µl aliquots of ethereal extracts of the samples or ethereal solutions of calibration standards are injected into the HPLC using a microsyringe. Concentrations of the compounds of interest are determined by comparing peak areas obtained for unknowns vs. calibration curves.

APPENDIX B

Methods For Preserving Wastewater Samples

This eliminates the interferences of H_2S and SO_2.

3) Oils and tars—These contain phenols. Perform an alkaline extraction before adding $CuSO_4$. Adjust sample pH to 12 to 12.5 by adding NaOH pellets. Extract oil and tar from the aqueous solution by CCl_4. Discard the oil- or tar-containing layer. Remove any excess of CCl_4 in the aqueous layer by warming on a water bath before proceeding with the distillation step.

3. Sampling

Sample domestic and industrial wastewaters in accordance with the instructions of Section 105.

4. Preservation and Storage of Samples

a. Phenols in concentrations usually encountered in wastewaters are subject to biological and chemical oxidation. Preserve and store samples unless they will be analyzed within 4 hr after collection.

b. Acidify to a pH of approximately 4.0 with H_3PO_4, using methyl orange or a pH meter. If H_2S or SO_2 is known to be present, briefly aerate or stir the sample with caution.

c. Add 1.0 g $CuSO_4 \cdot 5H_2O$/l sample to inhibit biodegradation of phenols.

d. Keep the sample cold (5 to 10 C). Analyze the preserved and stored samples within 24 hr after collection.

510 A. Distillation Step for Methods B and C

1. Principle

The phenols are distilled at a more or less constant rate from the nonvolatile impurities. The rate of volatilization of the phenols is gradual, so that the volume of the distillate must equal that of the sample being distilled. The use of $CuSO_4$ during distillation of an acidic sample permits the formation of cupric sulfide without subsequent decomposition to H_2S. The acidic solution also prevents the precipitation of cupric hydroxide, which acts as an oxidizing agent toward phenols.

2. Apparatus

a. Distillation apparatus, all-glass, consisting of a 1-l pyrex distilling apparatus with Graham condenser* (see Figure 318:1.)

b. pH meter.

3. Reagents

Prepare all reagents with distilled water free of phenols and chlorine.

a. Copper sulfate solution: Dissolve 100 g $CuSO_4 \cdot 5H_2O$ in distilled water and dilute to 1 l.

b. Phosphoric acid solution, 1+9: Dilute 10 ml 85% H_3PO_4 to 100 ml with distilled water.

c. Methyl orange indicator: Dissolve 0.5 g methyl orange in 1 l distilled water.

d. Special reagents for turbid distillates:

*Corning No. 3360 or equivalent.

PHENOLS/Chloroform Ex

1) *Sulfuric acid*, 1*N*.
2) *Sodium chloride.*
3) *Chloroform or et*
4) *Sodium hydroxi*

41.7 ml 6*N* NaOH t
solve 10 g NaOH in
water.

4. Procedure

a. Measure 500 m
beaker, lower the pH
4.0 with the 1+9 H_3P
the methyl orange in
meter, add 5 ml CuS
transfer to the distill
Use a 500-ml gradua
receiver. Omit addi
$CuSO_4$ if the sample
described in 510.4.

b. Distill 450 ml sar
tillation, and when boil
ml phenol-free distilled
tilling flask. Continue
total of 500 ml has bee

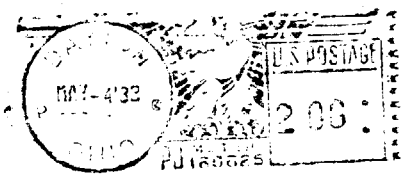
c. One distillation
sample adequately. O
ever, the distillate is tu
acidify the distillate w
add 5 ml $CuSO_4$ solu
described in ¶4*b* abo
distillate is still turbid,

510 B.

1. General Discus

a. Principle: The
phenols react with 4-a

*Similar in principle to, bu
ASTM D-1783-62 (Standar
adapted from E. EISENSTAEDT.
3:153.



Wright State University
DAYTON, OHIO 45435 .
Dr. Thomas O. Tiernan
Brehm Laboratory

Mr. Curtis Ross
US EPA
Region V
~~230 S. Dearborn~~ 536
Chicago, Illinois 60604

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P 286 035 695
MAIL